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Water adsorption on activated carbons with different degrees of oxidation

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A typical activated carbon, derived from olive stones, has been oxidized to different degrees with $(NH_4)_2S_2O_8$ and analysed by water vapour adsorption, immersion calorimetry, acid–base titration and temperature-programmed desorption of CO_2 and CO monitored by mass spectrometry. These techniques led to a coherent description of the surfaces and of their chemistry. The water adsorption isotherms, of type IV, were decomposed into type I and V contributions and analysed in terms of the Dubinin–Astakhov equation. The corresponding calculated enthalpies of immersion into water are in agreement with the experimental values. The number of carboxyl, lactone, phenol and basic groups identified by titration, can also be related to the parameters of the Dubinin–Astakhov equation and to the enthalpy of immersion into water. Finally, a good linear correlation is found between the amounts of CO_2 and CO desorbed from the surface, the enthalpies of immersion into water and the total number of sites identified on the surface.

Water vapour is often present in filtration processes and may affect the adsorption characteristics of the activated carbons. However, in view of the relatively low dispersion energy between water molecules and the graphene sheets, adsorption depends strongly on the presence of hydrophilic sites, or so-called primary centres. These are essentially oxygen surface complexes, where the formation of clusters begins by hydrogen bonding.

It is well known that oxygen surface complexes are formed on activated carbons when they are treated with oxidizing agents, either in the gas phase or in solution.[1–5] One method, to introduce predominantly acidic surface oxides, is to treat the activated carbons with different oxidizing solutions; however, this treatment can affect the surface area and the pore texture of the activated carbons. It has been reported, recently,[6] that activated carbons obtained from almond shells, on treatment with $(NH_4)_2S_2O_8$, produce stronger acid groups than with HNO_3, in spite of the fact that the latter creates larger amounts of oxygen surface complexes. Furthermore, there is the added advantage that treatment with $(NH_4)_2S_2O_8$, unlike that with HNO_3, does not modify the surface area and the porous texture of the original activated carbon significantly. The aim of this work is to study the adsorption of water vapour on activated carbons with different amounts of oxygen surface complexes, but with a similar pore texture, after treatment with $(NH_4)_2S_2O_8$. The chemistry of the surface groups and its relation to water adsorption will be examined in more detail.

The adsorption of water vapour by untreated activated carbons has been studied extensively and a mechanism was suggested by Dubinin *et al.*[7] and later by Dubinin and Serpinski.[8] The corresponding equation, describing type V isotherms in the range of relative pressures $0.3–0.4 < P/P_0 < 0.8$, is

$$P/P_0 = a/[c(a_0 + a)(1 - ka)] \quad (1)$$

where a represents the amount of water, usually in mmol g^{-1}, adsorbed at P/P_0; a_0 is the number of primary centres, characterized by the number of water molecules directly attached to them, implicitly a 1:1 ratio; k is a constant related to the total amount of water adsorbed at $P/P_0 = 1$ and c is the ratio between the rate constants of adsorption and desorption. As shown elsewhere,[9] c is related to the molar enthalpy of immersion into water, which provides a test for self-consistency between adsorption and immersion. The following empirical relation has been established by Stoeckli *et al.*[10] for the enthalpy of immersion of a number of untreated activated carbons into water,

$$\Delta_i H/\text{J g}^{-1} = -25a_0 - 0.6(a_s - a_0) \quad (2)$$

Here, the primary centres are probably of the carbonyl type, leading to desorption of CO at high temperature.

More recently, it has been shown by Stoeckli and co-workers[9,11,12] that water adsorption isotherms of types IV and V can also be described within the framework of Dubinin's theory. The fundamental relation is the Dubinin–Astakhov equation,[13,14] used to represent type I isotherms for adsorption by microporous solids

$$N_a = N_{a0} \exp[-(A/E)^n] \quad (3)$$

N_a represents the amount adsorbed at T and P/P_0; N_{a0} is the limiting amount in the micropores; $A = RT \ln(P_0/P)$; and E and n are temperature-invariant parameters of the system under investigation. For type I isotherms, corresponding to the filling of micropores by organic and many inorganic compounds, one can use a shifting factor, β, called the affinity coefficient, such that $E = \beta E_0$. β is dependent on the adsorptive.

It appears that the S-shaped isotherm of type V, observed for water on carbons with a low oxygen content,[11] is also described by the Dubinin–Astakhov equation. However, the characteristic energy, E, is much lower (1–2 kJ mol^{-1}) than for type I isotherms, where E is typically *ca.* 15–25 kJ mol^{-1}. For water isotherms of type V, the affinity coefficient, β, also loses its meaning and consequently one uses only E.

As shown previously,[12] for oxidized carbons the type IV water adsorption isotherm can be decomposed into two contributions, both of which follow the Dubinin–Astakhov eqn.

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(3): the first, at low relative pressures, is of type I and the second is of type V. The former has been associated with adsorption by acidic centres.[15] The second contribution, which can also be described by the Dubinin–Serpinski eqn. (1), corresponds to adsorption by hydrophilic centres, as found in activated carbons before oxidation, which are probably of the carbonyl type.[9,10]

As shown by Stoeckli and co-workers, on the basis of a thermodynamic treatment,[11,14] the enthalpy of immersion of a microporous carbon into a liquid, whose vapour is adsorbed according to eqn. (3), is

$$\Delta_i H/\mathrm{J\ g^{-1}} = -EN_{a0}(1 + \alpha T)\Gamma(1 + 1/n) \qquad (4)$$

where α is the thermal expansion coefficient of the liquid and Γ is the tabulated 'Gamma' function. The underlying assumption is the temperature-invariance of E and n, which has been verified for a number of water adsorption isotherms of types IV and V. Eqn. (3) and (4) can therefore be used in the present study.

Experimental

The activated carbons were obtained from olive stones; the raw material, with a particle size between 1 and 2 mm, was carbonized in an N_2 flow at 1273 K for 30 min. Activation in steam was carried out at 1103 K for 7 h, as described elsewhere.[16] This led to sample AZ46-0, which has a degree of activation of 46% and a relatively well developed microporous structure.

This carbon was subsequently oxidized with $(NH_4)_2S_2O_8$ for different periods of time. The procedure[6] was as follows: 1 g of solid was treated with 10 ml of a saturated solution of $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 at 298 K for periods of time varying between 1 and 24 h. After the treatment, the samples were washed with distilled water until absence of sulfates (as determined with $BaCl_2$) was reached. This produced the six samples referred to as AZ46-1 to AZ46-24, the last number giving the oxidation time in hours.

All samples were characterized by CO_2 adsorption at 273 K and cross-checked by immersion calorimetry[5,14] into CH_2Cl_2 at 293 K. Mercury porosimetry up to 3000 kg cm^{-2} gave the volume, V, of the pores larger than 4.9 nm. Temperature-programmed desorption (TPD) was carried out by heating the samples in an He flow up to 1273 K at a heating rate of 50 K min^{-1} and monitoring the amounts of CO and CO_2 with a mass spectrometer (Thermocube, from Balzers Ltd.), as described elsewhere.[17] The samples were also titrated with bases of different strengths (NaOH, Na_2CO_3 and $NaHCO_3$) following Boehm's method.[1] Since NaOH titrates carboxyl, lactones and phenolic groups, Na_2CO_3 titrates carboxyl and lactones and $NaHCO_3$ titrates only carboxylic groups, one can obtain the number of the different acid groups. The bases, also present on the surface, were titrated with HCl, as described earlier.[18]

Water adsorption was carried out at 298 K, using a gravimetric apparatus equipped with quartz springs. Prior to the adsorption runs, the samples were outgassed at 383 K for 24 h under a dynamic vacuum of 10^{-6} Torr. The adsorption isotherms were obtained after reaching the equilibrium for each point, *i.e.* after no discernible change in adsorption was observed. The equilibrium time, which depended on the sample and the region of the isotherm under investigation, could be as long as 2 to 3 days per point. For comparison purposes, another set of adsorption isotherms was determined by allowing an arbitrary equilibrium time of only 2 h for each point. It appears that, under such conditions, the initial part of the isotherm, the Langmuir type, is not observed. As a consequence, the mathematical analysis, described below, leads to results which are not consistent with other determinations, in particular, the values of the enthalpies of immersion.

Enthalpies of immersion into water were determined with a calorimeter of the Tian–Calvet type, as described elsewhere.[5,11,14]

Results and Discussion

The CO_2 adsorption isotherms obtained at 273 K were fitted to the Dubinin–Astakhov eqn. (3). This leads to the structural parameters W_0, E_0 and n given in Table 1. They are very similar, which indicates that oxidation with $(NH_4)_2S_2O_8$ does not modify the structure significantly with respect to the original carbon AZ46-0. This is also confirmed by the volumes, V, of the pores larger than 4.9 nm, of *ca.* 0.40 cm^3 g^{-1}.

The carbons have large micropores and are relatively heterogeneous,[5] since n is smaller than the usual value of 2. Immersion calorimetry into CH_2Cl_2 at 293 K confirms the CO_2 adsorption data and indicates the presence of an external surface area *ca.* 150 m^2 g^{-1}, which is reasonable for this type of activated carbon.

The amounts of CO and CO_2 evolved from the samples up to 1273 K are given in Table 1. As expected, these amounts increase with oxidation time, like the oxygen content of the samples (1.3 to 11.2%). The amounts of acid and base surface groups, m, obtained from titrations are shown in Table 1. Correlations between these properties, including immersion calorimetry, will be discussed below.

The water adsorption isotherms, measured at 298 K, are all of type IV. Fig. 1 shows those of the original sample (AZ46-0) and of the most activated sample (AZ46-24). As expected, the inflexion point is shifted towards lower relative pressures, P/P_0, and the initial section, of type I, increases with the degree of oxidation.[10,11] These modifications reflect directly the increase in oxygen surface complexes, since the structure of the original carbon is not affected by the oxidation. All isotherms show hysteresis loops at high and low relative pressures, which is typical for capillary condensation and for micropore filling by water.

As shown previously,[12] type IV adsorption isotherms can be regarded as the sum of a type I contribution at low relative pressures, and of a classical type V section, becoming important for $P/P_0 > 0.3$–0.4. This behaviour has been observed for a number of activated carbons[11,12,15,19–22] and Fig. 2 shows the result of the isotherm decomposition for samples AZ46-0, AZ46-4 and AZ46-24. The type I and type V isotherms can be

Table 1 Pore texture and surface chemistry of the activated carbons

sample	W_0 /cm^3 g^{-1}	E_0 /kJ mol^{-1}	n	V /cm^3 g^{-1}	CO /mmol g^{-1}	CO_2 /mmol g^{-1}	O[a] (%)	carb /meq g^{-1}	lac /meq g^{-1}	phe /meq g^{-1}	base /meq g^{-1}
AZ46-0	0.595	14.1	1.41	0.390	0.33	0.24	1.3	0.23	0.20	0.14	0.70
AZ46-1	0.586	14.0	1.47	0.394	2.16	0.83	6.1	0.48	0.32	0.42	0.27
AZ46-3	0.585	14.7	1.52	0.400	2.59	0.97	7.2	0.80	0.50	0.60	0.43
AZ46-4	0.586	14.7	1.49	0.400	2.72	1.04	7.7	0.95	0.55	0.53	0.55
AZ46-5	0.579	14.7	1.48	0.407	2.94	1.17	8.5	1.06	0.64	0.40	0.61
AZ46-10	0.565	14.5	1.42	0.388	3.64	1.46	10.5	1.28	0.94	0.18	0.69
AZ46-24	0.571	14.2	1.40	0.360	3.90	1.55	11.2	1.47	0.97	0.28	0.87

[a] From the amounts of CO and CO_2.

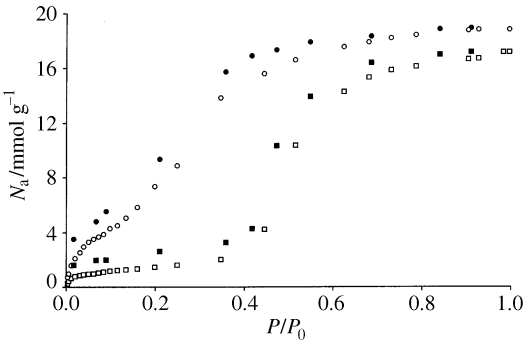

Fig. 1 Adsorption isotherms of water vapour at 298 K on activated carbons: (□) AZ46-0 and (○) AZ46-24. Open symbols adsorption and closed symbols desorption.

fitted to the Dubinin–Astakhov eqn. (3) and the corresponding parameters E, N_{a0} and n are given in Table 2.

Note that the characteristic energies E(I) obtained for the initial section (6.48–7.58 kJ mol^{-1}) are similar to those obtained for other carbons[12] subjected to different treatments. Assuming that the criteria of temperature-invariance of parameters E and n is also satisfied by the present series of carbons, it is possible to calculate, with eqn. (4), the formal contribution of the type I section to the enthalpy of immersion into water, $\Delta_i H$(I). As shown in Table 2, the quantity $-\Delta_i H(\mathrm{I})/N_{a0}(\mathrm{I})$ varies from 6.7 to 8.5 kJ mol^{-1}, in good agreement with earlier results.[12] It represents the average contribution to $\Delta_i H$ of the water molecules attached to the titrated sites. [It is assumed, implicitly, that N_{a0}(I) corresponds entirely to the saturation of the active sites by water].

Dubinin and co-workers[15] have observed that, for activated carbons oxidized in humid air at 673 K, N_{a0}(I) is close to the number of acidic sites, but this is not necessarily the case with other treatments. In the present study, the picture can be refined and it is possible to evaluate the number of water molecules, w_i, interacting with each type of site, since their numbers, m, are known from titrations (Table 1). A multiple linear regression following Newton's method and based on the mass balance shows that, for the seven carbons, the following relation holds,

$$N_{a0}(\mathrm{I})/\mathrm{mmol\ g^{-1}} = w_1 m(\mathrm{carb}) + w_2 m(\mathrm{lac}) + w_3 m(\mathrm{phe}) + w_4 m(\mathrm{base}) \quad (5)$$

with $w_1 = 2.81$, $w_2 = 2.74$, $w_3 = 1.40$ and $w_4 = 1.58$ and where m(carb), m(lac), m(phe) and m(base) represent the amounts of carboxyl, lactone, phenolic and basic surface groups.

This result, illustrated by Fig. 3, with a correlation coefficient of 0.9262, suggests that, within experimental error, there are *ca.* 3 water molecules interacting with the carboxyl and lactone groups, and 1.5 with the phenol and basic groups. Since the contribution of the type I section to the enthalpy of immersion into water, $\Delta_i H$(I), can be calculated through eqn. (4) (see also Table 2), it is possible to establish the energy balance associated with the various surface groups. The data for the seven samples were fitted to the equation

$$\Delta_i H(\mathrm{I})/\mathrm{J\ g^{-1}} = h_1 m(\mathrm{carb}) + h_2 m(\mathrm{lac}) + h_3 m(\mathrm{phe}) + h_4 m(\mathrm{base}) \quad (6)$$

where $h_1 = 17.4$, $h_2 = 17.5$, $h_3 = 9.5$ and $h_4 = 10$ kJ eq^{-1}. The correlation is illustrated in Fig. 4 (correlation coefficient of 0.8940).

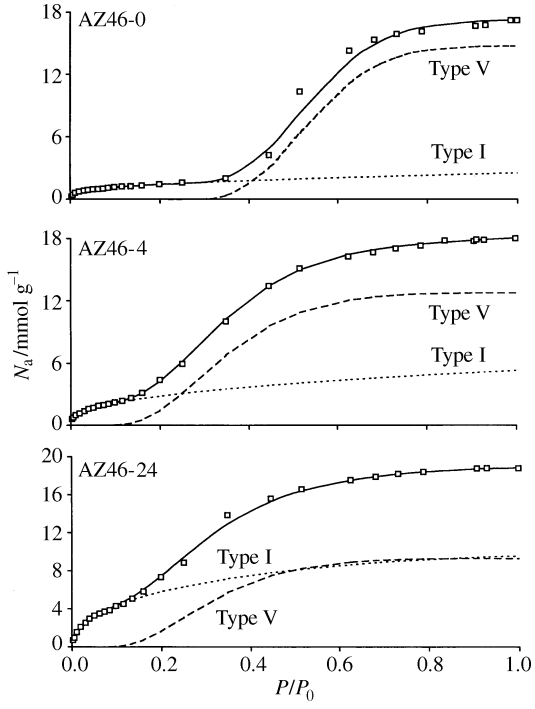

Fig. 2 Adsorption isotherms of water vapour at 298 K and their decomposition in Dubinin–Astakhov isotherms of types I and V (only the adsorption branch is shown)

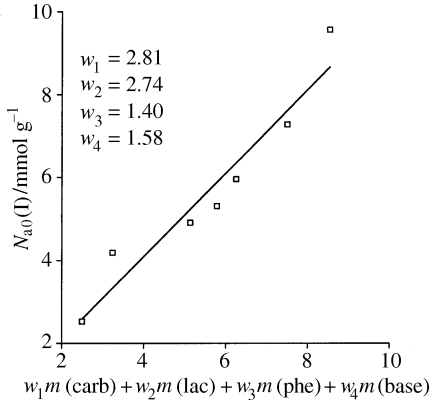

Fig. 3 N_{a0}(I) *vs.* $w_1 m$(carb) + $w_2 m$(lac) + $w_3 m$(phe) + $w_4 m$(base). The quantities w_1–w_4 denote the number of water molecules attached to the corresponding site.

Table 2 Dubinin–Astakhov equation analysis of the overall water vapour adsorption isotherms at 298 K by the activated carbons

	initial section (type I)					second section (type V)							
sample	n	E(I) /kJ mol^{-1}	N_{a0}(I) /mmol g^{-1}	$-\Delta_i H$(I) /J g^{-1}	$-\Delta_i H(\mathrm{I})/N_{a0}(\mathrm{I})$ /kJ mol^{-1}	n	E(V) /kJ mol^{-1}	N_{a0}(V) /mmol g^{-1}	$-\Delta_i H$(V) /J g^{-1}	N_{a0} (total) /mmol g^{-1}	$-\Delta_i H_{total}$ /J g^{-1}		$-\Delta_i H_{exp}$ /J g^{-1}
AZ46-0	0.89	7.54	2.52	21.37	8.48	3.19	1.74	14.67	24.34	17.19	45.71	(23.12)[a]	31.7
AZ46-1	1.19	7.58	4.18	31.80	7.61	2.64	2.55	13.41	32.35	17.59	64.16		—
AZ46-3	1.08	6.80	4.90	34.45	7.03	3.01	2.80	12.75	33.94	17.65	68.39		78.9
AZ46-4	0.98	6.48	5.30	36.88	6.96	2.94	3.08	12.75	37.30	18.05	74.18	(43.95)	—
AZ46-5	0.99	6.81	5.95	43.32	7.28	3.23	3.08	12.10	35.55	18.05	78.87		—
AZ46-10	1.21	6.68	7.27	48.54	6.68	3.35	3.05	10.96	31.95	18.23	80.48		—
AZ46-24	1.29	6.91	9.55	64.99	6.81	3.00	3.36	9.30	29.71	18.85	94.70	(54.21)	94.0

[a] Values of $-\Delta_i H_{total}$, in parentheses, were obtained from the isotherms under non-equilibrium conditions, leaving an arbitrary time of 2 h for each point.

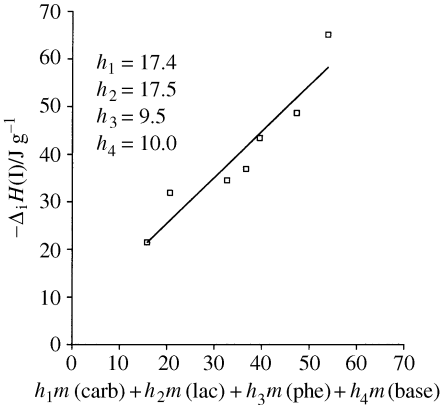

Fig. 4 $\Delta_i H(I)$ *vs.* $h_1 m(carb) + h_2 m(lac) + h_3 m(phe) + h_4 m(base)$. The quantities h_1–h_4 denote the contributions from the water molecules attached to the sites.

From eqn. (5) and (6) it follows that the specific contributions h_i/w_i of the water molecules attached to the groups are similar and vary from -6.2 to -6.8 kJ mol^{-1}.

Note that, during oxidation with $(NH_4)_2S_2O_8$, the surface groups do not follow the same trends (see Table 1). Whereas the carboxyls and the lactones increase steadily, the phenols tend to decrease after an initial rise. This confirms the earlier observation[23] that the phenolic groups are oxidized when oxidation lasts beyond 3 h. On the other hand, the bases titrated with HCl remain relatively constant after an initial decrease.

These results show that a coherent picture can be obtained from the first section of the water adsorption isotherm and its relation to the enthalpy of immersion.

As expected,[12] for the second part of the water isotherms, of type V, a much lower value of E is obtained than for the initial section. It reflects the less favourable adsorption mechanism, which begins on inert primary centres, and the subsequent filling of the micropore volume. As a consequence, the contribution to the enthalpy of immersion, $\Delta_i H(V)$, calculated from eqn. (4), is lower and corresponds to that observed typically for untreated activated carbons.[5,10] As discussed earlier,[12] the descriptions of the type V section, either by the Dubinin–Serpinski eqn. (1) or the Dubinin–Astahkov eqn. (3), are not exclusive. The former has the advantage that it leads to the number of primary centres, a_0. Both approaches also provide estimates for the enthalpies of immersion, through eqn. (2) and (4). Table 3 shows the corresponding results, which are in good agreement. Note that the type V sections of all oxidized samples are similar, with a number of primary centres, a_0, near 0.90 mmol g^{-1}, given by the Dubinin–Serpinski eqn. (1).

As shown in Table 2, there is a good agreement between the calculated enthalpy of immersion into water, $\Delta_i H(total) = \Delta_i H(I) + \Delta_i H(V)$ and the experimental values, which confirms the validity of the approach based on the decomposition of the overall isotherm of type IV.[12] However, as mentioned before, the true adsorption equilibrium must be attained. If this is the case, it is possible to extend eqn. (6) to the total enthalpy of immersion, which is directly accessible by calorimetry. An overall fit for the seven samples considered in this study leads to

$$\Delta_i H_{total}/J\ g^{-1} = 15.0\ m(carb) + 15.0\ m(lac) + 8.8\ m(phe) + 9.1\ m(base) + 21.5\ a_0 + 21.6 \quad (7)$$

The correlation is illustrated in Fig. 5 (with a correlation coefficient of 0.9076). The results for the individual groups are close to those of eqn. (2) and (6), which shows self-consistency. The last term, 21.6 J g^{-1}, corresponds closely to the filling of the micropores and to the wetting of the external surface area, $0.6[a_s - N_{a0}(I) - a_0]$ and 0.030 J m^{-2} m^2 g^{-1}, respectively.

Finally, it appears that the amounts of CO and CO_2 desorbed from the seven solids (Table 1), a_1 and a_2, respectively can be related to the enthalpies of immersion into water through the simple equation

$$-\Delta_i H_{total}/J\ g^{-1} = 6.5a_1 + 17.6a_2 + 38 \quad (8)$$

illustrated by Fig. 6 (with a correlation coefficient of 0.9436). This observation is not too surprising, since the total amount of CO and CO_2 desorbed from the surface corresponds to the sum of the functions titrated with NaOH and HCl plus the primary centres, a_0, of the type V section, as shown in Table 3. (The only exception is the original carbon AZ46-0, for which one finds a discrepancy). Eqn. (8) must, therefore, be compatible with eqn. (7), through the overall mass-balance. The last term of eqn. (8) depends on the non-specific part of the enthalpy of immersion.

The correlation illustrated by eqn. (8) has also been confirmed by preliminary TPD studies of activated carbons, described earlier,[24] which had been oxidized with HNO_3. The corresponding results will be presented later. It is also interesting to point out the observation of Bradley *et al.*,[25] showing a linear correlation between the enthalpy of immersion into water of commercial carbon blacks and the oxygen content of the surface. It is directly related to eqn. (8).

In conclusion, we have shown that the combination of water adsorption analysis, immersion calorimetry, the titra-

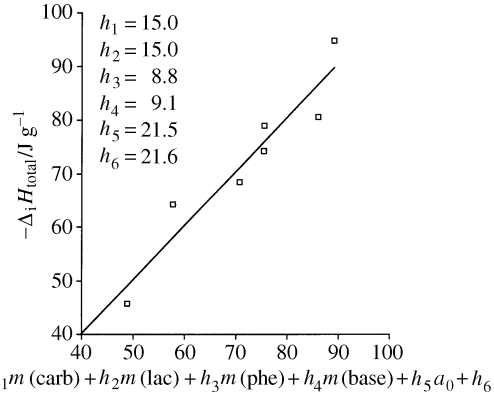

Fig. 5 $\Delta_i H(total)$ *vs.* $h_1 m(carb) + h_2 m(lac) + h_3 m(phe) + h_4 m(base) + h_5 a_0 + h_6$

Table 3 Data from the Dubinin–Serpinski and Dubinin–Astakhov models applied to type V

sample	a_0 /mmol g^{-1}	a_s /mmol g^{-1}	c	$-\Delta_i H(V)$/J g^{-1} eqn. (4)	$-\Delta_i H(V)$/J g^{-1} eqn. (2)	CO + CO_2[a] /mmol g^{-1}	NaOH + HCl + a_0[b] /mmol g^{-1}
AZ46-0	0.62	17.19	2.55	24.34	16.82	0.57	1.91
AZ46-1	0.84	17.59	4.06	32.35	23.25	2.96	2.49
AZ46-3	0.95	17.65	4.45	33.94	26.50	3.56	3.41
AZ46-4	1.01	18.05	5.50	37.30	28.18	3.76	3.80
AZ46-5	0.90	18.06	5.16	35.55	26.07	4.11	3.87
AZ46-10	1.09	18.23	5.30	31.95	31.25	5.10	4.13
AZ46-24	0.96	18.85	7.00	29.71	29.65	5.45	4.58

[a] Amount of CO + CO_2 desorbed. [b] Total amount of surface sites.

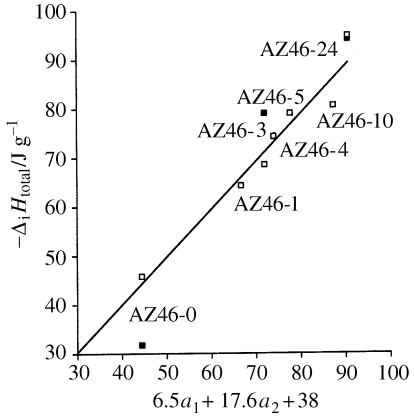

Fig. 6 $\Delta_i H_{exp}$ *vs.* $6.5a_1 + 17.6a_2 + 3.8$; where a_1 and a_2 are the amounts of CO and CO_2 desorbed, respectively. (■) Experimental values of the enthalpy of immersion.

tion of chemical groups and the TPD of activated carbons oxidized with $(NH_4)_2S_2O_8$ leads to consistent results. The study also emphasises the importance of immersion calorimetry and water adsorption by microporous carbons, in relation to the Dubinin–Astakhov equation.

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